

# Adapted Gaussian Basis Sets for Atoms Cs to Lr Based on the Generator Coordinate Hartree–Fock Method

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**ABSTRACT:** We have applied a discretized version of the generator coordinate Hartree–Fock method to generate adapted Gaussian basis sets for atoms Cs ( $Z = 55$ ) to Lr ( $Z = 103$ ). Our Hartree–Fock total energy results, for all atoms studied, are better than the corresponding Hartree–Fock energy results attained with previous Gaussian basis sets. For the atoms Cs to Lr we have obtained an energy value within the accuracy of  $10^{-4}$  to  $10^{-3}$  hartree when compared with the corresponding numerical Hartree–Fock total energy results. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 858–865, 1998

**Keywords:** generator coordinate Hartree–Fock method; adapted Gaussian basis sets; total energy

## Introduction

There is a considerable degree of freedom in choosing the basis functions for atomic and molecular calculations as any complete set of functions can be employed. The choice of the basis set in nonrelativistic atomic and molecular calculations is crucial as it determines the computational cost and the accuracy of the calculations.

Hartree–Fock (HF) calculations are carried out with nuclei represented as particle points. In this case, Slater-type functions (STF) have the correct functional form to describe the nonrelativistic wave

function of atoms at the origin, but they are not particularly suitable for analytic self-consistent field (SCF) molecular calculations. On the other hand, Gaussian-type functions (GTF) are useful in the evaluation of multicenter integrals in molecules, but they do not possess the correct functional behavior at the origin.

The generator coordinate Hartree–Fock (GCHF) method was introduced in 1986,<sup>1</sup> and one of its first applications was in the generation of GTF and STF universal basis sets for the first and second rows of the period table.<sup>2,3</sup> The GCHF method was recently tested successfully in the generation of universal Gaussian basis sets (UGBS) for the atoms H ( $Z = 1$ ) through La ( $Z = 57$ ),<sup>4</sup> and for the heavy atoms from Ce ( $Z = 58$ ) through Lr ( $Z = 103$ ).<sup>5</sup> It is important to mention that the first unique set of

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exponents for various different atoms was the even-tempered STF basis of Silver et al.<sup>6</sup>

Here we show that we can improve the HF total energy results for Cs through Lr previously<sup>4,5</sup> obtained by just using the GCHF method with the aim to generate an adapted basis set (a specific basis set for each atom in study), instead of a universal basis set, as has been done with the previous applications of the GCHF method.<sup>2-5</sup> To do this we employ the GCHF method in such a way that the best numerical integration of the Griffin–Wheeler–HF (GWHF) equations [see eq. (2)] is searched individually for each atom studied, and therefore, the integration of the GWHF equations is not performed with a universal basis set in mind.

## Generation of Adapted Gaussian Basis Sets

The GCHF method is the result of employing the generator coordinate (GC) ansatz<sup>7</sup> for the independent particle model; that is:

$$\psi_i(1) = \int \phi_i(1, \alpha) f_i(\alpha) d\alpha, \quad i = 1, \dots, n \quad (1)$$

where  $n$  is the number of one-electron functions of the system,  $\phi_i$  are the generator functions (GTF in the present application),  $f_i$  the weight functions, and  $\alpha$  the generator coordinate. The variation of the total energy expectation value,  $E$ , produces the GWHF equations:

$$\int [F(\alpha, \beta) - \varepsilon_i S(\alpha, \beta)] f_i(\beta) d\beta = 0, \quad i = 1, \dots, n \quad (2)$$

where  $\varepsilon_i$  are the HF eigenvalues, and  $F(\alpha, \beta)$  and  $S(\alpha, \beta)$  are, respectively, the Fock and overlap kernels (see ref. 1 for more details about these kernels).

The GWHF equations [eq. (2)] are integrated through discretization with a technique that preserves the integral character of the GCHF method; that is, integral discretization (ID).<sup>8</sup> The ID technique is implemented with a relabeling of the generator coordinate space; that is:

$$\Omega = \frac{\ln \alpha}{A}, \quad A > 1 \quad (3)$$

where  $A$  is a scaling parameter determined numerically. Then, the generator coordinate,  $\Omega$ , is discretized (for each symmetry) in an equally spaced mesh  $\{\Omega_k\}$  so that:

$$\Omega_k = \Omega_{\min} + (k - 1) \Delta\Omega, \quad k = 1, \dots, N \quad (4)$$

In eq. (4),  $N$  corresponds to the number of discretization points, where  $N$  defines the GTF basis set size, and  $\Delta\Omega$  an increment. The lowest value,  $\Omega_{\min}$  (initial point), and the highest value,  $\Omega_{\max} = \Omega_{\min} + (N - 1) \Delta\Omega$ , are chosen so as to encompass adequately, the integration range of  $f(\Omega)$ .

Because the GWHF equations are obtained from the minimization of the functional,  $E$ , with respect to the weight functions,  $f_i$ , the description of  $f_i$  governs the quest for the total energy for any atomic system. Achieving the best HF energy for an atomic system means obtaining the best description of  $f_i$  through the numerical approximation just outlined. The quest for the best weight function associated with any atomic orbital is implemented by the ID, and the discretization parameters,  $\Omega_{\min}$ ,  $\Delta\Omega$ , and  $N$ , are responsible for attaining the best weight function. The ID approach contrasts to the procedure of optimizing orbital exponents, common in HF–Roothaan calculations; that is, variational discretization (VD). An extensive discussion about these two approaches (ID and VD) and their applications in two problems having exact solutions (the harmonic oscillator and the hydrogen atom) is given in ref. 8.

## Results and Discussion

The HF SCF calculations are performed, for atoms Cs to Lr (except for atoms with atomic numbers  $Z = 91, 92, 93, 96$ , and  $97$ ), by employing the GTF exponents generated with the GCHF method.<sup>1</sup> The vector coupling coefficients used in the calculations on the open-shell configurations has been taken from the tabulation by Malli and Olive.<sup>9</sup> These tables show the vector coupling coefficients for the electron configurations  $s$ ,  $p^n$ ,  $sp^n$ ,  $d^n$ ,  $sd^n$ ,  $p^m d^n$ ,  $sp^m d^n$ , and  $f^n$ . The HF ground-state total energy results for atoms with  $Z = 58, 64, 91, 92, 93, 96$ , and  $97$  are not calculated here, because the ground-state electron configurations of these atoms have open  $d$  and  $f$  shells. Only for Ce ( $Z = 58$ ) and Gd ( $Z = 64$ ) we have calculated the total energy of excited states ( $^3H$  and  $^7F$ , respectively), because, in these cases, we have the numerical HF (NHF) results of Fischer<sup>10</sup> for which to compare.

The GTF exponents generated in this work can be easily reproduced by using eqs. (3) and (4) and Table I. The discretization parameters,  $\Omega_{\min}$  (initial point),  $\Delta\Omega$  (increment), and  $N$  (number of basis function exponents), for each of the  $s$ ,  $p$ ,  $d$ , and  $f$

symmetries are shown in Table I for each atom studied in this work. To obtain the optimized exponents used here, we start with the discretization parameters used for the generation of the UGBS exponents<sup>5</sup>:  $\Omega_{\min}(s) = -0.540$ ,  $\Omega_{\min}(p) =$

TABLE I.  
Discretization Parameters<sup>a</sup> of Adapted Gaussian Basis Sets (AGBS).

Z	Atom	N	s		p		d		f	
			$\Omega_{\min}$	$\Delta\Omega$	$\Omega_{\min}$	$\Delta\Omega$	$\Omega_{\min}$	$\Delta\Omega$	$\Omega_{\min}$	$\Delta\Omega$
55	Cs	(31s21p14d)	-0.687	0.119	-0.368	0.113	-0.133	0.113	—	—
56	Ba	(32s21p14d)	-0.627	0.116	-0.356	0.112	-0.110	0.112	—	—
57	La	(31s23p18d)	-0.630	0.118	-0.386	0.105	-0.490	0.109	—	—
58	Ce	(32s22p16d10f)	-0.660	0.112	-0.430	0.111	-0.294	0.112	-0.290	0.129
59	Pr	(32s22p16d10f)	-0.646	0.113	-0.410	0.110	-0.139	0.105	-0.276	0.129
60	Nd	(31s22p16d11f)	-0.631	0.116	-0.402	0.110	-0.139	0.105	-0.285	0.122
61	Pm	(31s22p16d11f)	-0.626	0.116	-0.394	0.110	-0.132	0.105	-0.275	0.122
62	Sm	(31s22p16d11f)	-0.615	0.118	-0.385	0.110	-0.117	0.106	-0.261	0.122
63	Eu	(32s22p16d11f)	-0.649	0.113	-0.381	0.110	-0.122	0.105	-0.249	0.122
64	Gd	(31s22p16d11f)	-0.609	0.117	-0.346	0.108	-0.106	0.105	-0.239	0.121
65	Tb	(32s22p16d11f)	-0.658	0.116	-0.321	0.106	-0.094	0.104	-0.240	0.122
66	Dy	(31s22p16d11f)	-0.600	0.119	-0.364	0.110	-0.234	0.111	-0.239	0.122
67	Ho	(31s22p16d12f)	-0.620	0.115	-0.352	0.110	-0.194	0.107	-0.259	0.117
68	Er	(32s22p16d12f)	-0.601	0.112	-0.358	0.110	-0.188	0.108	-0.251	0.117
69	Tm	(32s22p17d12f)	-0.606	0.112	-0.343	0.110	-0.305	0.109	-0.248	0.117
70	Yb	(32s22p17d12f)	-0.596	0.112	-0.337	0.110	-0.298	0.109	-0.239	0.116
71	Lu	(31s23p18d12f)	-0.663	0.119	-0.448	0.110	-0.442	0.111	-0.204	0.115
72	Hf	(31s22p17d12f)	-0.556	0.119	-0.310	0.109	-0.415	0.113	-0.170	0.114
73	Ta	(31s22p18d12f)	-0.580	0.114	-0.307	0.109	-0.415	0.110	-0.147	0.113
74	W	(31s22p18d12f)	-0.615	0.117	-0.414	0.111	-0.398	0.110	-0.121	0.112
75	Re	(31s22p18d12f)	-0.580	0.115	-0.417	0.112	-0.388	0.110	-0.108	0.112
76	Os	(32s22p17d12f)	-0.558	0.113	-0.415	0.112	-0.350	0.111	-0.092	0.111
77	Ir	(32s22p18d13f)	-0.552	0.112	-0.395	0.111	-0.366	0.109	-0.119	0.108
78	Pt	(32s23p18d13f)	-0.548	0.112	-0.395	0.110	-0.374	0.109	-0.140	0.109
79	Au	(32s22p18d12f)	-0.541	0.112	-0.269	0.108	-0.366	0.110	-0.045	0.109
80	Hg	(32s22p17d12f)	-0.540	0.113	-0.261	0.108	-0.301	0.111	-0.036	0.109
81	Tl	(31s23p18d12f)	-0.470	0.114	-0.514	0.112	-0.289	0.105	-0.011	0.108
82	Pb	(31s24p17d12f)	-0.445	0.115	-0.506	0.111	-0.251	0.110	0.004	0.108
83	Bi	(32s24p17d12f)	-0.514	0.112	-0.481	0.110	-0.232	0.109	0.026	0.108
84	Po	(31s23p17d13f)	-0.415	0.112	-0.473	0.111	-0.221	0.109	-0.039	0.105
85	At	(31s23p18d12f)	-0.396	0.112	-0.466	0.111	-0.303	0.107	0.045	0.107
86	Rn	(32s24p17d12f)	-0.493	0.112	-0.448	0.108	-0.197	0.108	0.061	0.104
87	Fr	(32s24p18d13f)	-0.659	0.116	-0.427	0.107	-0.263	0.106	0.018	0.100
88	Ra	(33s23p18d14f)	-0.635	0.114	-0.354	0.109	-0.268	0.106	-0.119	0.105
89	Ac	(32s24p19d13f)	-0.640	0.115	-0.401	0.106	-0.438	0.109	0.009	0.104
90	Th	(33s24p19d13f)	-0.587	0.112	-0.365	0.105	-0.423	0.109	0.003	0.102
94	Pu	(32s24p19d14f)	-0.607	0.113	-0.353	0.105	-0.191	0.101	-0.260	0.112
95	Am	(32s24p19d14f)	-0.604	0.115	-0.345	0.105	-0.185	0.101	-0.247	0.111
98	Cf	(32s24p19d14f)	-0.597	0.114	-0.328	0.105	-0.305	0.105	-0.231	0.111
99	Es	(33s25p19d14f)	-0.582	0.112	-0.320	0.103	-0.173	0.101	-0.226	0.111
100	Fm	(32s25p19d14f)	-0.600	0.116	-0.394	0.104	-0.273	0.103	-0.215	0.110
101	Md	(33s25p19d14f)	-0.589	0.114	-0.389	0.104	-0.278	0.104	-0.209	0.110
102	No	(32s25p19d14f)	-0.596	0.115	-0.386	0.104	-0.268	0.104	-0.203	0.110
103	Lr	(32s25p19d14f)	-0.583	0.115	-0.385	0.104	-0.407	0.109	-0.183	0.109

<sup>a</sup>The scaling parameter value [see eq. (3)] used for all symmetries of all atoms (Cs to Lr) is equal to  $A = 6.0$ .

TABLE II. Hartree-Fock Total Energies in Hartree (Sign Reversed) of Atoms Cs (Z = 55) through Lr (Z = 103).

Z	Atom	Configuration	State	AGBS size	AGBS <sup>a</sup>	UGBS size	UGBS <sup>b</sup>	GGBS size	GGBS <sup>c</sup>	Numerical <sup>d</sup>
55	Cs	[Xe]6s(1)	<sup>2</sup> S	31s21p14d	7553.932767	28s19p14d	7553.926073 <sup>e</sup>	32s25p17d	7553.932485	7553.933658
56	Ba	[Xe]6s(2)	<sup>1</sup> S	32s21p14d	7883.543011	27s19p14d	7883.536790 <sup>e</sup>	32s25p17d	7883.542832	7883.543827
57	La	[Xe]6s(2)5d(1)	<sup>2</sup> D	31s23p18d	8221.066126	28s19p14d	8221.055819 <sup>e</sup>	32s25p20d	8221.065624	8221.066703
58	Ce	[Xe]6s(2)4f(2)	<sup>3</sup> H	32s22p16d10f	8566.918727	32s22p16d10f	8566.915116	—	—	8566.9196 <sup>f</sup>
59	Pr	[Xe]6s(2)4f(3)	<sup>4</sup> I	32s22p16d10f	8921.180270	32s22p16d10f	8921.176919	32s25p17d16f	8921.180179	8921.181028
60	Nd	[Xe]6s(2)4f(4)	<sup>5</sup> I	31s22p16d11f	9283.882095	31s22p16d11f	9283.879207	32s25p17d16f	9283.881730	9283.882944
61	Pm	[Xe]6s(2)4f(5)	<sup>6</sup> H	31s22p16d11f	9655.098041	31s22p16d11f	9655.095389	32s25p17d16f	9655.097658	9655.098969
62	Sm	[Xe]6s(2)4f(6)	<sup>7</sup> F	31s22p16d11f	10034.95158	31s22p16d11f	10034.94902	32s25p17d16f	10034.95126	10034.95255
63	Eu	[Xe]6s(2)4f(7)	<sup>8</sup> S	32s22p16d11f	10423.54213	32s22p16d11f	10423.53966	32s25p17d16f	10423.54170	10423.54302
64	Gd	[Xe]6s(2)4f(8)	<sup>7</sup> F	31s22p16d11f	10820.61615	31s22p16d11f	10820.61376	—	—	10820.617 <sup>f</sup>
65	Tb	[Xe]6s(2)4f(9)	<sup>6</sup> H	32s22p16d11f	11226.56733	31s22p16d11f	11226.56456	33s26p18d16f	11226.56732	11226.56837
66	Dy	[Xe]6s(2)4f(10)	<sup>5</sup> I	31s22p16d11f	11641.45104	31s22p16d11f	11641.44876	33s26p18d16f	11641.45090	11641.45260
67	Ho	[Xe]6s(2)4f(11)	<sup>4</sup> I	31s22p16d12f	12065.28842	31s22p16d12f	12065.28623	32s24p17d14f	12065.28824	12065.28980
68	Er	[Xe]6s(2)4f(12)	<sup>3</sup> H	32s22p16d12f	12498.15155	32s22p16d12f	12498.14947	32s24p17d14f	12498.15112	12498.15278
69	Tm	[Xe]6s(2)4f(13)	<sup>2</sup> F	32s22p17d12f	12940.17313	32s22p17d12f	12940.17154	32s24p17d14f	12940.17256	12940.17440
70	Yb	[Xe]6s(2)4f(14)	<sup>1</sup> S	32s22p17d12f	13391.45486	32s22p17d12f	13391.45325	32s24p17d14f	13391.45423	13391.45619
71	Lu	[Xe]6s(2)4f(14)5d(1)	<sup>2</sup> D	31s23p18d12f	13851.80627	32s22p17d12f	13851.80163	31s24p20d14f	13851.80597	13851.80800
72	Hf	[Xe]6s(2)4f(14)5d(2)	<sup>3</sup> F	31s22p17d12f	14321.24759	32s22p17d12f	14321.24418	31s24p20d14f	14321.24756	14321.24981
73	Ta	[Xe]6s(2)4f(14)5d(3)	<sup>4</sup> F	31s22p18d12f	14799.81083	31s22p17d12f	14799.80815	31s24p20d14f	14799.81058	14799.81260
74	W	[Xe]6s(2)4f(14)5d(4)	<sup>5</sup> D	31s22p18d12f	15287.54433	32s22p17d12f	15287.54302	31s24p20d14f	15287.54401	15287.54637
75	Re	[Xe]6s(2)4f(14)5d(5)	<sup>6</sup> S	31s22p18d12f	15784.53106	31s22p17d12f	15784.52976	31s24p20d14f	15784.53083	15784.53319
76	Os	[Xe]6s(2)4f(14)5d(6)	<sup>5</sup> D	32s22p17d12f	16290.64632	32s22p17d12f	16290.64466	32s24p20d15f	16290.64615	16290.64860
77	Ir	[Xe]6s(2)4f(14)5d(7)	<sup>4</sup> F	32s22p18d13f	16806.11140	32s22p18d13f	16806.11067	32s24p20d15f	16806.11031	16806.11315

78	Pt	[Xe]6s(1)4f(14)5d(9)	<sup>3</sup> D	32s23p18d13f	17331.06850	32s23p18d13f	17331.06713	32s24p20d15f	17331.06739	17331.06996
79	Au	[Xe]6s(1)4f(14)5d(10)	<sup>2</sup> S	32s22p18d12f	17865.39850	32s23p17d13f	17865.39723	32s24p20d15f	17865.39726	17865.40008
80	Hg	[Xe]6s(2)4f(14)5d(10)	<sup>1</sup> S	32s22p17d12f	18409.98954	32s23p17d13f	18408.98906	32s24p20d15f	18408.98771	18408.99149
81	Tl	[Xe]6s(2)4f(14)5d(10)6p(1)	<sup>2</sup> P	31s23p18d12f	18961.82224	32s23p18d13f	18961.81863	31s25p18d13f	18961.82160	18961.82482
82	Pb	[Xe]6s(2)4f(14)5d(10)6p(2)	<sup>3</sup> P	31s24p17d12f	19524.00593	32s23p17d13f	19524.00301	31s27p18d13f	19524.00458	19524.00804
83	Bi	[Xe]6s(2)4f(14)5d(10)6p(3)	<sup>4</sup> S	32s24p17d12f	20095.58460	32s23p17d13f	20095.58177	32s27p17d13f	20095.58342	20095.58643
84	Po	[Xe]6s(2)4f(14)5d(10)6p(4)	<sup>3</sup> P	31s23p17d13f	20676.49858	32s23p18d13f	20676.49741	31s27p17d13f	20676.49740	20676.50091
85	At	[Xe]6s(2)4f(14)5d(10)6p(5)	<sup>2</sup> P	31s23p18d12f	21266.87953	32s23p18d13f	21266.87815	32s27p19d13f	21266.87870	21266.88171
86	Rn	[Xe]6s(2)4f(14)5d(10)6p(6)	<sup>1</sup> S	32s24p17d12f	21866.77048	32s24p17d13f	21866.76857	32s27p19d13f	21866.77224	21866.77224
87	Fr	[Rn]7s(1)	<sup>2</sup> S	32s24p18d13f	22475.85637	32s24p18d14f	22475.84828	—	—	22475.85871
88	Ra	[Rn]7s(2)	<sup>1</sup> S	33s23p18d14f	23094.30140	33s23p18d14f	23094.29522	—	—	23094.30367
89	Ac	[Rn]7s(2)6d(1)	<sup>2</sup> D	32s24p19d13f	23722.18912	32s24p18d14f	23722.17716	—	—	23722.19206
90	Th	[Rn]7s(2)6d(2)	<sup>3</sup> F	33s24p19d13f	24359.61985	33s25p19d14f	24359.60899	—	—	24359.62244
94	Pu	[Rn]7s(2)5f(6)	<sup>7</sup> F	32s24p19d14f	27008.71608	32s25p19d14f	27008.71075	—	—	27008.71944
95	Am	[Rn]7s(2)5f(7)	<sup>6</sup> S	32s24p19d14f	27695.88405	32s25p19d14f	27695.87876	—	—	27695.88722
98	Cf	[Rn]7s(2)5f(10)	<sup>5</sup> I	32s24p19d14f	29817.41491	32s25p19d14f	29817.41034	—	—	29817.41892
99	Es	[Rn]7s(2)5f(11)	<sup>4</sup> I	33s25p19d14f	30544.96919	33s25p19d14f	30544.96419	—	—	30544.97219
100	Fm	[Rn]7s(2)5f(12)	<sup>3</sup> H	32s25p19d14f	31282.77367	32s25p19d14f	31282.76778	—	—	31282.77760
101	Md	[Rn]7s(2)5f(13)	<sup>2</sup> F	33s25p19d14f	32030.92954	33s25p19d14f	32030.92448	—	—	32030.93297
102	No	[Rn]7s(2)5f(14)	<sup>1</sup> S	32s25p19d14f	32789.50792	32s25p19d14f	32789.50336	—	—	32789.51214
103	Lr	[Rn]7s(2)5f(14)6d(1)	<sup>2</sup> D	32s25p19d14f	33557.94506	32s25p19d14f	33557.93826	—	—	33557.95041

<sup>a</sup>HF total energies obtained by using our adapted Gaussian basis sets (AGBS).

<sup>b</sup>HF total energies obtained by using universal Gaussian basis sets (ref. 5).

<sup>c</sup>HF total energies obtained by using geometric Gaussian basis sets (ref. 12).

<sup>d</sup>Numerical HF total energies obtained from ref. 11.

<sup>e</sup>HF total energies obtained by using universal Gaussian basis sets (ref. 4).

<sup>f</sup>Numerical HF total energies obtained from ref. 10.

$-0.428$ ,  $\Omega_{\min}(d) = -0.316$ ,  $\Omega_{\min}(f) = -0.204$ , and  $\Delta\Omega = 0.112$  (the last parameter has the same value for all symmetries and atoms studied in ref. 5). Then, we use increments of 0.001, first in the parameter  $\Omega_{\min}(s)$ , keeping all others fixed, until finding the lowest HF total energy value. Next, we repeat the procedure for the parameter  $\Delta\Omega(s)$ , now for the optimum value of  $\Omega_{\min}(s)$  and still keeping the remaining parameters with the initial values. The process is continued until reaching the last parameter [ $\Delta\Omega(f)$ ] in Table I, and then successively repeated from the beginning until the total energy stabilizes within ten significant figures. The optimum scaling parameter  $A$  [see eq. (3)] found in all calculations was 6.0. A typical case that occurs in Table I is, for example, that for  $s$  symmetry the initial point of Fr ( $-0.659$ ) is lower than the corresponding initial point of Rn ( $-0.493$ ); this is a consequence of the entrance of one electron in the Fr  $7s$  atomic orbital, making this symmetry more diffuse.

Table II shows the HF total energy results for atoms from Cs to Lr (except for atoms with  $Z = 91, 92, 93, 96$ , and  $97$ ) computed with our adapted Gaussian basis sets (AGBS) by employing the GCHF method. Our results are compared with the corresponding results obtained previously by using the UGBS,<sup>4,5</sup> with NHF results obtained by Koga et al.<sup>11</sup> and the NHF results of Fischer,<sup>10</sup> and with the geometrical Gaussian basis sets (GGBS) results of Clementi et al.<sup>12</sup> (noting that Clementi had only generated GGBS for  $Z$  up to 86). Our AGBS for Cs–Rn are always smaller in size than the GGBS size,<sup>12</sup> and for Cs–Lr are equal or smaller in size than the UGBS size,<sup>4,5</sup> except for Cs, Ba, La, Tb, Lu, Ta, and Re atoms, where we have used a slightly larger basis set size than the corresponding one used in refs. 4 and 5. We can see from Table II that the HF energy results obtained with our AGBS are always better than those obtained with the UGBS.<sup>4,5</sup> This result is not surprising because we have employed the GCHF method in such a way that the best numerical integration of the GWHF equations [see eq. (2)] is searched individually for each atom studied here, whereas in refs. 4 and 5 the numerical integration was performed for a universal basis set (an extensive discussion about UGBS and AGBS is presented in ref. 4).

We can also see from Table II that our HF energy values are always lower than the corresponding ones obtained with the GGBS.<sup>12</sup> We call attention to the fact that the GGBS is also an adapted basis set (one different set of GTF expo-

nents for each atom studied). Thus, we may conclude that our approach (the GCHF method), to generate AGBS for Cs through Rn, is more efficient than the approach used by Clementi et al.,<sup>12</sup> because we have optimized for each symmetry of each atom studied here both the  $\Omega_{\min}$  and  $\Delta\Omega$  parameters that appear in eq. (4), whereas other works<sup>12</sup> have optimized for each symmetry of each atom only the  $\alpha$  parameter of the even-tempered formula ( $\zeta_k = \alpha\beta^{k-1}$ ,  $k = 1, \dots, N$ ), making  $\beta$  constant for all symmetries of an atom. We attribute the high numerical accuracy of our AGBS to the ID technique of the GCHF method, because, with this technique, the Gaussian function exponents are generated by the discretization of the integral GWHF equations with the best numerical integration for each atom as a goal.

Moreover, we can also see from Table II that for Cs through Gd we have obtained with our AGBS, when compared to the corresponding NHF results, HF energy values within the accuracy of  $10^{-4}$  hartree; furthermore, for Tb through Lr, the HF energy differences, when also compared with the corresponding NHF results, are of a few millihartree.

In Table III we present the HF orbital energies ( $\epsilon$ ) obtained for the Eu atom by using our AGBS (the second column), the GGBS (the third column) generated by Clementi et al.,<sup>12</sup> and by using a NHF method (the fourth column). We can see that for all orbitals our values are slightly lower than the corresponding results obtained with the GGBS; furthermore, our values are systematically closer to the NHF results than the values obtained by Clementi et al.<sup>12</sup>

The AGBS presented here for the atoms Cs ( $Z = 55$ ) through Lr ( $Z = 103$ ), despite the importance of relativistic effects in these atoms, can be used easily as a starting basis set in relativistic calculations. This procedure was first employed by Matsuoka and Huzinaga<sup>13</sup> who showed that orbital exponents optimized through the well-tempered scheme for nonrelativistic atoms (i.e., orbital exponents obtained from a nonrelativistic environment) can be carried over to relativistic calculations to produce wave functions close to the relativistic HF limit. There is a lot of relativistic atomic calculations in the literature using the Matsuoka and Huzinaga recipe.<sup>14–17</sup> Here we emphasize that all these relativistic atomic calculations<sup>13–17</sup> use large Gaussian basis sets.

Mohanty and Clementi<sup>15</sup> used GGBS optimized for the nonrelativistic case (see ninth column of Table II) augmented in the number of functions to

**TABLE III.**  
**Hartree–Fock Orbital Energies ( $\varepsilon$ , in Hartree) of the Eu Atom ( $Z = 63$ ).**

Orbital	$\varepsilon$ (AGBS) <sup>a</sup>	$\varepsilon$ (GGBS) <sup>b</sup>	$\varepsilon$ (Numerical) <sup>c</sup>
1s	−1690.696188	−1690.695224	−1690.696544
2s	−272.315603	−272.314761	−272.315849
3s	−61.311650	−61.310909	−61.311967
4s	−12.744297	−12.743669	−12.744771
5s	−1.815846	−1.815103	−1.816028
6s	−0.170903	−0.170683	−0.170964
2p	−258.362556	−258.361705	−258.362798
3p	−55.073529	−55.072759	−55.073825
4p	−10.245769	−10.245037	−10.246171
5p	−1.065244	−1.064484	−1.065486
3d	−43.602328	−43.601547	−43.602595
4d	−5.779656	−5.778929	−5.780046
4f	−0.711354	−0.710634	−0.711724
HF total energy	−10423.54213	−10423.54170	−10423.54302

<sup>a</sup>This work (using our adapted Gaussian basis set).  
<sup>b</sup>Geometrical Gaussian basis set (ref. 12).  
<sup>c</sup>Numerical Hartree–Fock results.

calculate Dirac–Fock (DF) total energies for the atoms from He through Rn. They verified that, for all atoms, it was possible to find a basis set that gave energies within a few millihartree of the numerical values. Therefore, we can also use our large AGBS, generated here in a relativistic approach, to calculate DF energies; for example, Dirac–Fock–Breit (DFB) orbital energies, in this case, assuming Koopman’s theorem, to estimate ionization potentials (IP) of an atomic system, and then they can be compared with the corresponding experimental values of IP.

Recently, Malli et al.<sup>16</sup> contracted a large Gaussian basis set (32s29p20d17f) generated in a non-relativistic environment, to report *ab initio* all-electron DF and DFB SCF calculations for XeF<sub>2</sub>, XeF<sub>4</sub>, and ThF<sub>4</sub> (see refs. 18–20, respectively) and assessed the effects of relativity and electron correlation in the electronic structure, dissociation energy, bonding, etc., for these systems. For XeF<sub>2</sub> and XeF<sub>4</sub>, their results<sup>18,19</sup> showed that the values of the Xe–F bond lengths and dissociation energies for these molecules are in excellent agreement with the corresponding experimental values. Therefore, the accurate basis sets presented in this work represent a starting point for future relativistic studies of molecules containing the heavy atoms studied. Experimental molecular properties, such as dissociation energy, equilibrium internuclear separa-

tion, IP, and vibrational frequency, for these systems, can be better described through theoretical calculations when an accurate basis set is employed.

### Conclusions

The HF total energy values reported in this work for atoms from Cs ( $Z = 55$ ) to Lr ( $Z = 103$ ) show that a specific and careful numerical evaluation of the GWHF integral equations in the GCHF formalism for each atom is able to generate highly accurate basis sets to be used as a starting basis set for future relativistic atomic and molecular calculations involving the heavy atoms studied. Due to the accuracy of our basis sets, we think that experimental atomic and molecular properties will probably be better described through relativistic theoretical calculations.

The accuracy of the HF total energy results obtained with our AGBS represents an achievement that has not been obtained so far with finite basis set expansion of GTF in HF calculations. For all atoms studied, the HF energy values obtained in this work with the GCHF method are competitive with the corresponding ones obtained by NHF calculations. The AGBS generated in this work can also be considered more accurate than the UGBS previously presented in the literature.

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